

Method Of Fabricating Patterned Polymer Film With Nanometer Scale

Inventors: Seung-Man YANG
Se Gyu JANG
Dae-Geun CHOI

Background Of The Invention

Field of the Invention

[0001] The present invention relates to preparation methods of regular polymer patterns for the fabrication of small electronic and optical devices, and methods of fabricating a nano-patterned polymer film, characterized in that polymer patterns having nanometer sized line widths therebetween (which are difficult to realize by a photolithography or electron beam process) can be quickly and inexpensively fabricated at desired positions by use of a self-assembling process and a soft lithography process.

Related Art

[0002] Research on new fabrication processes for fine patterns having 100 nanometer or less scale, instead of a conventional photolithography process, has been a subject of much interest recently. Miniaturization and high integration of semiconductor devices result in decreasing manufacturing time and cost, and improve performance. However, when using a conventional semiconductor photolithography process, it is difficult to fabricate patterns having line widths of 100 nanometer or less, because of the limitation of the photolithographic resolution.

[0003] Therefore, electron beam lithography or X-ray lithography have been used to obtain such fine patterns. Although these methods result in finer line widths and higher resolution compared to photolithography, they require expensive equipment and long processing periods.

[0004] Further, a soft lithography process has been proposed as an alternative patterning method, in which a soft material such as polydimethylsiloxane is used as a mask to form the pattern. This has the advantages of inexpensive

costs and short processing periods (see *Angew. Chem. Int. Ed.* 37:550 (1998); *Appl. Phys. Lett.* 63:2002 (1993); *J. Am. Chem. Soc.* 124:1676 (2002); *Langmuir* 19:1963 (2003); *Nano lett.* 2:347 (2002); *Langmuir* 18:5314 (2002); *Macromolecules* 33:3042 (2000)).

[0005] However, for the soft lithography process, sizes and line widths of the resulting patterns are defined by the size and shape of an original master. To manufacture the original fine master, electron beam lithography has to be used.

[0006] To solve the above problems, formation methods of nano-patterns that use a self-assembling process of nanoparticles have been proposed. The self-assembling process is advantageous in terms of controllable sizes and intervals of the pattern according to the selection of the particles, low fabrication costs and short periods required for fabrication of the desired patterns. However, conventional methods of forming the nano-patterns have a problem in that desired patterns cannot be prepared at desired positions by only self-assembly (see *Chem. Mater.* 11:2322 (1999); *Science* 287:2240 (2000); *Nature* 414:293 (2001); *Adv. Mater.* 14:930 (2002); *Chem. Commun.* 982 (2003); *Adv. Mater.* 15:703 (2003); *Langmuir* 12:4033 (1996); *Appl. Phys. Lett.* 78:2273 (2001)).

Summary Of The Invention

[0007] Therefore, it is an object of the present invention to alleviate the problems encountered in the related art and to provide a method of fabricating a patterned polymer film with nanometer scale, characterized in that polymer patterns having nanometer sized line widths therebetween (which are difficult to realize by a photolithography or electron beam process) can be rapidly and inexpensively fabricated at desired locations by use of a self-assembling process and a soft lithography process.

[0008] According to a first embodiment of the present invention, there is provided a method of fabricating a patterned polymer film comprising filling particles of a predetermined size in a pattern provided to a soft polymer mold to prepare an embossed stamp, placing the embossed stamp on a desired

polymer film, allowing the stamp to stand at temperatures higher than a glass transfer temperature of the polymer film for a predetermined time, and releasing the embossed stamp from the polymer film.

[0009] In another embodiment of the present invention, there is provided a method of fabricating a patterned polymer film comprising filling particles of a predetermined size in a pattern provided to a soft polymer mold to prepare an embossed stamp, placing the embossed stamp on a coating layer of a polymer precursor formed on a substrate, curing the coating layer, and releasing the embossed stamp from the cured coating layer.

Brief Description Of The Drawings

[0010] **FIG. 1** is a sectional view showing a process of sequentially fabricating a nano-patterned polymer film of the present invention.

[0011] **FIG. 2A** is an electron micrograph of a polydimethylsiloxane mold replicated on a master.

[0012] **FIG. 2B** is an optical micrograph of the polydimethylsiloxane mold replicated on the master.

[0013] **FIG. 3A** is an electron micrograph of a stamp including spherical particles self-assembled into a 300 nm sized pattern of the mold.

[0014] **FIG. 3B** is an electron micrograph of the stamp including spherical particles self-assembled into a 400 nm sized pattern of the mold.

[0015] **FIG. 3C** is an electron micrograph of the stamp including spherical particles self-assembled into a 600 nm sized pattern of the mold.

[0016] **FIG. 3D** is an electron micrograph of the stamp including spherical particles self-assembled into a 900 nm sized pattern of the mold.

[0017] **FIG. 3E** is an electron micrograph of the stamp including spherical particles self-assembled into a 1800 nm sized pattern of the mold.

[0018] **FIG. 3F** is an electron micrograph of the stamp including spherical particles self-assembled to the mold without any pattern.

[0019] **FIG. 4A** is an electron micrograph of a patterned porous polymer replicated by the stamp of **FIG. 3C** using a UV curing process.

[0020] **FIG. 4B** is an electron micrograph of the patterned porous polymer replicated by the stamp of **FIG. 3D** using a UV curing process.

[0021] **FIG. 4C** is an electron micrograph of the patterned porous polymer replicated by the stamp of **FIG. 3E** using a UV curing process.

[0022] **FIG. 4D** is an electron micrograph of the patterned porous polymer replicated by the stamp of **FIG. 3F** using a UV curing process.

[0023] **FIG. 5A** is an electron micrograph of the spherical particles patterned in polyurethane, obtained by using the stamp of **FIG. 3D**.

[0024] **FIG. 5B** is an electron micrograph of the spherical particles patterned in polyurethane, obtained by using the stamp of **FIG. 3E**.

[0025] **FIG. 6A** is an electron micrograph of a porous polymer pattern replicated by the stamp of **FIGS. 3A and 3B** using a nano-imprinting process.

[0026] **FIG. 6B** is an electron micrograph of the porous polymer pattern replicated by the stamp of **FIG. 3C** using a nano-imprinting process.

[0027] **FIG. 6C** is an electron micrograph of the porous polymer pattern replicated by the stamp of **FIG. 3E** using a nano-imprinting process.

[0028] **FIG. 6D** is an electron micrograph of the porous polymer pattern replicated by the stamp of **FIG. 3F** using a nano-imprinting process.

Detailed Description Of The Invention

[0029] In some embodiments of the present invention, in order to fabricate a patterned polymer film, particles of a predetermined size are filled in a pattern of a soft polymer mold, so as to prepare an embossed stamp. Then, the embossed stamp is placed on a host polymer film, and allowed to stand at temperatures higher than a glass transfer temperature of the polymer film for a predetermined time. The embossed stamp is then removed from the polymer film.

[0030] Alternatively, a patterned polymer film is obtained by filling particles of a predetermined size in a pattern of a soft polymer mold, so as to prepare an embossed stamp. The embossed stamp is then placed on a coating layer of a polymer precursor, which is formed on a substrate. Thereafter, the coating

layer is cured, and the embossed stamp is released from the cured coating layer.

[0031] The soft polymer mold usable in the present invention is replicated from a master patterned with a predetermined shape, which is obtained by a soft lithography process exemplified by replica molding (see *Angew. Chem. Int. Ed.* 37:550 (1998); *Adv. Mater.* 9:147 (1997)), imprinting (*Nature* 417:835 (2002); *J. Vac. Sci. Technol. B.* 16:3825 (1998)), micromolding in capillary (*Nature* 376:581 (1995)), transfer molding (*Adv. Mater.* 8:837 (1996)), decal transfer molding (*J. AM. Chem. Soc.* 124:13583 (2002)), and solvent assisted micromolding (*Adv. Mater.* 9:6517 (1997)).

[0032] Various materials, such as quartz, glass, metal plates, and polymer soft materials can be used as the substrate or patterned master, in addition to a silicon wafer for a conventional photolithography process. The polymer soft material has a predetermined strength at room temperature and stable properties in an aqueous solution, and includes, for example, polystyrene, polyurethane, polymethylmethacrylate, polyimide, etc.

[0033] The patterning of the master material can be performed by using an electron beam (see *Appl. Phys. Lett.* 62:1499 (1993); *Nano Lett.* 2:43 (2002)) or photolithography (*Semiconductor International* 54 (1998); *Optics & Photonic News* 7:29 (1996)). As such, the pattern is not limited to any particular shape, and can be prepared in a desired shape, as required for the manufacturing process.

[0034] The material for use in the soft polymer mold is not particularly limited, so long as it has a predetermined strength at room temperature and is stable in an aqueous solution. The material can be, for example, polydimethylsiloxane, polyurethane, epoxy, polystyrene, polyimide, polyacrylonitrile, polymethylmethacrylate, polyurea, and mixtures thereof.

[0035] Although the particles filled in the pattern of the soft polymer mold are not particularly limited, they can have monodisperse properties and uniform sizes, with strength at room temperature. The particles can be, e.g., polymer beads, metallic materials, ceramics, and mixtures thereof. Of the above particles, the polymer beads have monodispersive particles with strength at

room temperature, and are not particularly limited so long as they are suitable for self-assembling and patterning. Examples of the polymer beads include polystyrene, polymethylmethacrylate, polyacrylate, polyurea, polyurethane, epoxy, polydimethylsiloxane, polyacrylamide, polyvinylalcohol, polybutadiene, polypropylene, polyethylene, polyethyleneoxide, and copolymers thereof. The metallic materials are not particularly limited so long as they satisfy the above requirements. The metallic materials are exemplified by inorganic metals, such as titanium, aluminum, iron, gold, cadmium sulfide, lead sulfide, lead chloride, copper, silica, etc.

[0036] The sizes and shapes of the particles are not particularly limited so long as they can be filled in the desired pattern. Thus, the particles with diameters ranging from several micrometers down to hundreds of nanometers can be used, depending on the size of the pattern.

[0037] The filling process of the particles into the engraved pattern is not particularly limited, and includes dip coating which disperses the particles into the solution (*Langmuir*. 12:1303 (1996)), spin coating (*J. Phys. Chem. B.* 103:3854 (1999); *Appl. Phys. A* 63:617 (1996)), or flowing by capillary force (*Phys. Rev. Lett.* 84:2997 (2000); *Chem. Commun.* 2507 (2000)).

[0038] The soft polymer mold filled with the particles is used as a stamp to obtain a polymer pattern. The filled particles protrude in a predetermined pattern from the surface of the soft polymer mold, resulting in the fine polymer pattern according to nano-imprinting or replica molding.

[0039] In some embodiments of the present invention, the stamp is positioned on the polymer film, and allowed to stand at temperatures higher than a glass transfer temperature of the used polymer for a predetermined time. Thereby, an engraved porous pattern is formed on the polymer film.

[0040] In this case, the usable polymer film materials are not particularly limited, and can be, for example, polystyrene, polymethylmethacrylate, polyacrylate, polyurea, polyurethane, epoxy, polydimethylsiloxane, polyacrylamide, polyvinylalcohol, polybutadiene, polypropylene, polyethylene, polyethyleneoxide, and copolymers thereof.

[0041] In some embodiments of the present invention, the stamp is positioned on the substrate coated with the polymer precursor, after which the polymer precursor is cured by heat or UV treatment, to form the engraved porous pattern on the polymer film. Alternatively, the stamp can be first placed on the substrate, and then the polymer precursor can be applied and cured.

[0042] To obtain the engraved fine polymer pattern, the self-assembled particles in the patterned mold should be stably maintained without being disordered upon the pattern transfer. To accomplish this, a polymer impregnation-prevention layer can be coated onto the stamp. Materials for the polymer impregnation-prevention layer are not particularly limited, and can include gold, silver, palladium, copper, chromium, titanium, and mixtures thereof. The polymer impregnation-prevention layer functions to prevent the particles of the stamp from releasing upon the pattern transfer, attributed to complete impregnation of the polymer into the particles.

[0043] **FIG. 1** is a sectional view showing a patterned soft polymer mold **102**. The mold **102** is prepared from a silicon master, which is usually manufactured using an electron beam or photolithography process by the replica molding of the soft lithography process.

[0044] The soft polymer mold **102** is composed of polydimethylsiloxane. A stamp **104** is provided with the self-assembled nanoparticles **106** by filling a dispersion of the monodisperse nanoparticles **106** into channels **108** of the soft polymer mold **102** using a self-assembly process. As such, in cases where the particles **106** and the mold **102** have the same polarity charge, the particles **106** are absent from the surface of the mold **102** due to repulsive force, and are arrayed into the engraved channels of the pattern by the capillary force. Here, the particles **106** can include silica nanoparticles. A gold layer **105** can be used to cover the stamp **104** and the particles **106**, to act as an impregnation-prevention layer.

[0045] For nano-imprinting (embossing), a polymer film **110** is formed on a substrate **102**, such as glass or a semiconductor wafer, using a spin coating process. Then, the stamp **104** is placed on the polymer film **110** and allowed to stand at temperatures higher than a glass transfer temperature of the

polymer film 110 ($T > T_g$), thus inducing fluidity of the polymer film 110. After a predetermined time, the stamp 104 is released from the polymer film 110, and thus an engraved polymer film 110A having a predetermined pattern. In such a case, the polymer film 110A can include polystyrene.

[0046] Alternatively, in order to prepare the polymer film directly patterned by the replica molding, polymer precursor 114 is coated on the substrate 112, and the stamp 104 is placed on the polymer precursor 114. Thereafter, the polymer precursor 114 is cured by heat or UV, thereby obtaining the desired engraved polymer pattern shown in **FIG. 1**. There, a polyurethane (PU) precursor 114 is used, and a UV curing process is used for curing the precursor 114.

[0047] The fabricating method of the present invention shown in **FIG. 1** has the following advantages, compared to a conventional “top-down” process by photolithography or electronic beam lithography, and a conventional “bottom-up” process using only self-assembly of particles.

[0048] First, it is possible to achieve fine patterning with line widths between lines of 100 nanometer or less, which is difficult to achieve by a conventional photolithography process. Further, such fine patterning can be rapidly and easily achieved by a simpler process than electron beam lithography. Also, the polymer pattern of the present invention can be easily fabricated with a gradient that is impossible to realize by a conventional semiconductor process. The polymer pattern also can have the line widths of various sizes, depending on the selected particles. In particular, the method described above can be repeatedly performed in a short period if there is the master, resulting in mass fabrication of the desired polymer pattern.

[0049] Second, the pattern described above has fewer drawbacks than conventional patterns resulting from only the self-assembly of particles. Moreover, in the present invention, only desired portions can be patterned.

[0050] Third, there are few limitations on materials that can be used, while a conventional process requires specific material restrictions and expensive processing steps.

[0051] Having generally described this invention, a further understanding can be obtained by reference to the examples which are provided herein for purposes of illustration only and are not intended to be limiting.

Example 1

Preparation of Engraved Porous Polymer Pattern by Replica Molding

[0052] To fabricate a soft polymer mold having line widths of various sizes, a quartz master produced by electron beam lithography process was used. First, polydimethylsiloxane (PDMS) as a soft polymer material was poured on the master and then cured at 80°C for 1 hour. **FIG. 2A** is an electron micrograph of the PDMS mold, which was poured to the master, replicated and then completely cured. **FIG. 2B** is an optical micrograph of the same PDMS mold, which displays different colors (in this figure, as shades of gray) by being scattered by various line widths.

[0053] Thereafter, particles were filled into the patterned soft polymer mold through a dip coating process. As such, the particles included spherical silica particles having a uniform size of 300 nm. The dip coating process was performed at 200 nm/sec. Further, since the dip coating was determined by surface tension and speed, the above parameters should be optimized for particular process parameters.

[0054] **FIGS. 3A to 3E** are photographs of the stamp, including nanoparticles and the soft polymer mold, formed by self-assembling the 300 nm sized spherical silica particles in channels having various sizes of the soft polymer mold. **FIG. 3F** is a photograph showing a monolayer of the particles self-assembled on the soft polymer mold without channels.

[0055] Moreover, a polyurethane precursor was allowed to flow between the stamp and the substrate using a capillary force, upon preparation of the polymer pattern by the replica molding. The polyurethane precursor was

cured under 410 nm UV for 20 min. When the polyurethane precursor was completely cured, the stamp was released from the polyurethane polymer. **FIGS. 4A to 4D** are electron micrographs of the porous polyurethane fabricated by the replica molding process using the stamp, in which the stamp was previously coated with a gold film (see **FIG. 1**) to prevent the impregnation of the polymer precursor up to the lower portions of the stamp, thus obtaining the engraved porous polyurethane film having the shapes complementary to those of the particles, as shown in **FIGS. 4A to 4D**.

Example 2

Preparation of Complex Pattern of Polymer and Particles by Replica Molding

[0056] Example 2 was prepared similar to Example 1, with the exception that the gold film was not coated on the stamp. In cases where the stamp was not coated (with the gold film serving to prevent the impregnation of the polymer precursor into the stamp), all the particles were separated from the stamp and buried in the polyurethane polymer film. Therefore, as shown in **FIGS. 5A** and **5B**, a complex pattern of embossed silica particles and polymer results resulted, instead of the engraved polymer pattern.

Example 3

Preparation of Polymer Pattern by Nano-imprinting (Embossing)

[0057] Before the nano-imprinting process, about 1 μm sized polystyrene film was spin-coated onto a silicon wafer and then dried. On the polystyrene coating layer, the gold film-coated stamp shown in **FIGS. 3A to 3F** was placed and allowed to stand at temperatures higher than a glass transfer temperature of 110°C, at which the polystyrene began to flow. After a

predetermined time, the stamp was released, and the engraved porous polystyrene patterns shown in **FIGS. 6A to 6D** were obtained.

[0058] As described hereinbefore, the present invention provides a method of fabricating a patterned polymer film on a nanometer scale. This is advantageous in that polymer patterns having nanometer sized line widths therebetween, which are difficult to realize by a photolithography or electron beam process, can be quickly and inexpensively fabricated at desired positions by use of a self-assembling process and a soft lithography process.

Conclusion

[0059] While various embodiments of the present invention have been described above, it should be understood that they have been presented by way of example only, and not limitation. It will be apparent to persons skilled in the relevant art that various changes in form and detail can be made therein without departing from the spirit and scope of the invention. Thus, the breadth and scope of the present invention should not be limited by any of the above-described exemplary embodiments, but should be defined only in accordance with the following claims and their equivalents.

[0060] All documents cited herein are hereby incorporated by reference in their entirety to the same extent as if each individual document was specifically and individually indicated to be incorporated by reference in its entirety.